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## **Silver in geological fluids from in situ X-ray absorption spectroscopy and first-principles molecular dynamics**

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# Supplementary Electronic Information

## Electronic annex 1

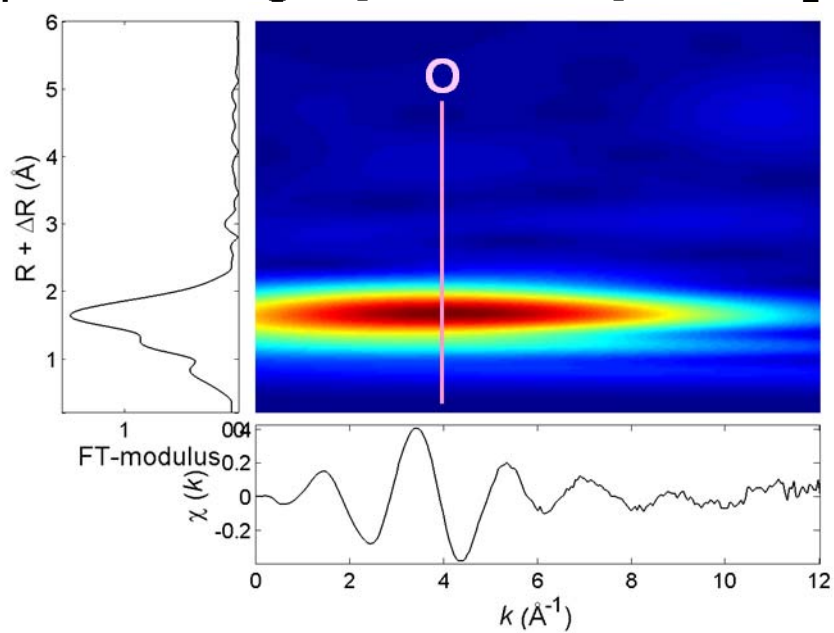
### Continuous Cauchy Wavelet Transform analysis of EXAFS spectra of selected Ag-chloride and nitrate solutions

**Supplementary Figure EA-1.** Continuous Cauchy Wavelet Transform analysis (CCWT, Munoz et al., 2003) of selected Ag K-edge EXAFS spectra of silver nitrate and silver chloride solutions at 600 bar and indicated temperature and composition, recorded in this study. Each graph represents  $k^2$ -weighted experimental spectrum, its Fourier Transform magnitude, and CCWT modulus showing the localization of each EXAFS contribution in  $(k, R)$  space. The color intensity is proportional to the magnitude of the CCWT modulus (blue to dark-blue = low, red to brown = high). The vertical lines indicate the maximum intensity positions for O and Cl neighbors around the Ag absorber. It can be seen in Fig. EA1-1A that these maximum intensity positions in both  $k$ - and  $R$ -space are distinctly different for O and Cl atoms around Ag, thus allowing clear identification of the presence of these backscatterers in the experimental spectrum. It can be seen in Fig. EA1-1B and EA-1C that no oxygen contribution is detected in all studied Cl-bearing solutions in a wide  $T$  (200-450°C) and total Cl concentration range (0.7-6.0 mol/kg), and that the signal is dominated by Cl backscatterers. Note, that with increasing Cl content (e.g., Fig. EA1-1B) and decreasing temperature (Fig. 1C), the shape of CCW Transform becomes wider and less symmetrical, indicating larger disorder in the Ag-Cl distances at high  $m_{Cl}$  and low  $T$ . This is in agreement with quantitative EXAFS fits showing the increase of DW factors and anharmonic cumulant  $c_3$  parameter (Table 1). This is in line with the presence of different silver chloride complexes at low  $T$  and high chlorinity as suggested by available solubility studies (Seward, 1976).

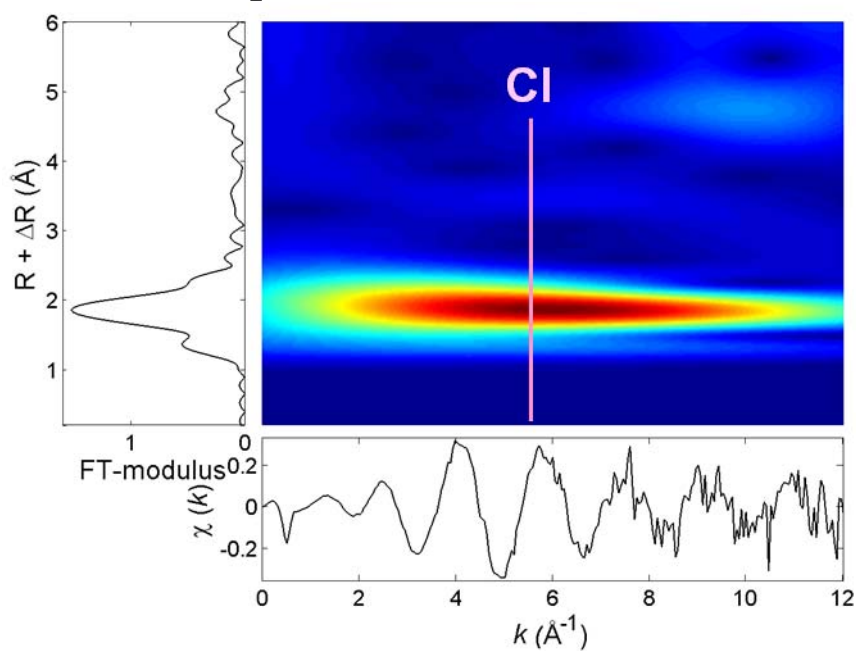
#### References for Electronic annex 1

- Munoz, M., Argoul, P., Farges F., 2003. Continuous cauchy wavelet transform analyses of EXAFS spectra: a qualitative approach. *Amer. Mineral.* 88, 694-700.
- Seward T.M. (1976) The stability of chloride complexes of silver in hydrothermal solutions up to 350°C. *Geochim. Cosmochim. Acta* 40, 1329-1341.

**exp #1, 0.21m AgNO<sub>3</sub>-0.10m HNO<sub>3</sub>-0.10m H<sub>2</sub>O<sub>2</sub>, 30°C**

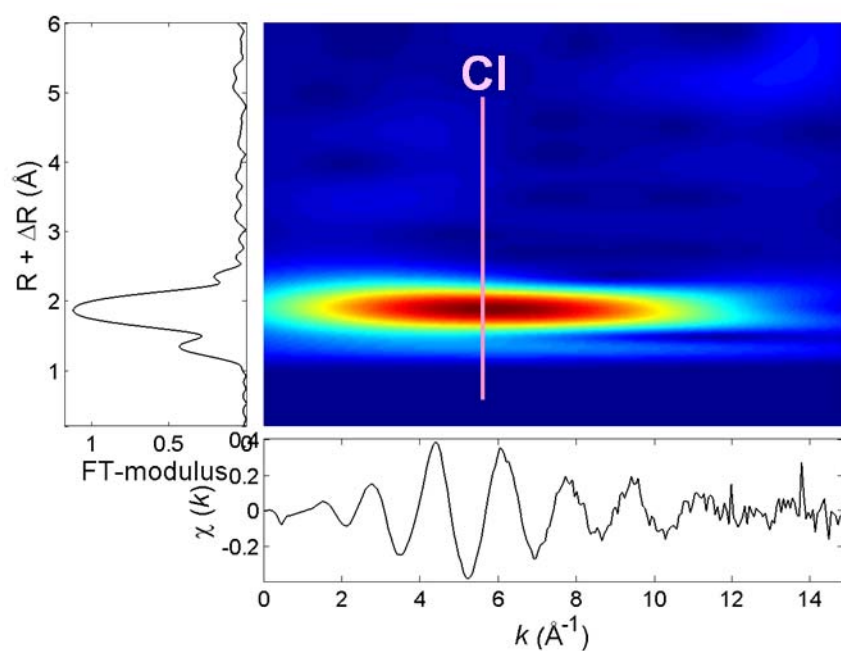


**exp #4, 0.18m AgCl-2.34m NaCl-0.12m HCl-0.10m H<sub>2</sub>O<sub>2</sub>, 200°C**

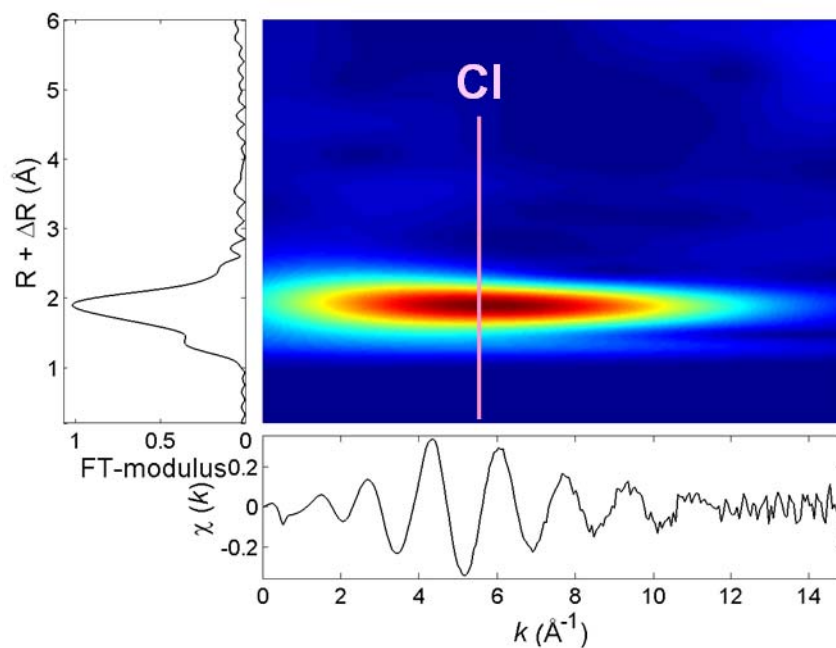


**Fig. EA1-1A**

**exp #6, 0.17m AgCl-0.42m NaCl-0.11m HCl-0.06m H<sub>2</sub>O<sub>2</sub>, 400°C**

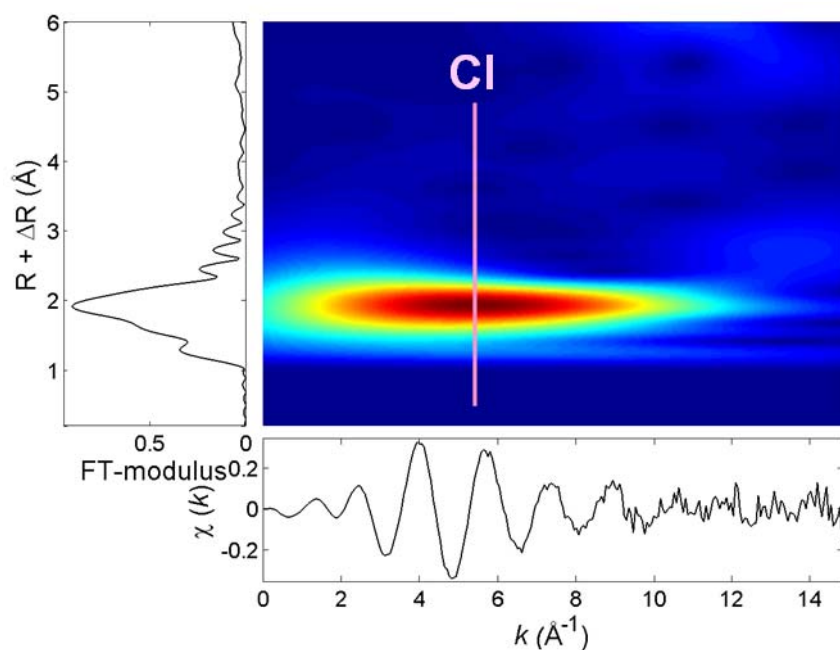


**exp #4, 0.18m AgCl-2.34m NaCl-0.12m HCl-0.06m H<sub>2</sub>O<sub>2</sub>, 400°C**

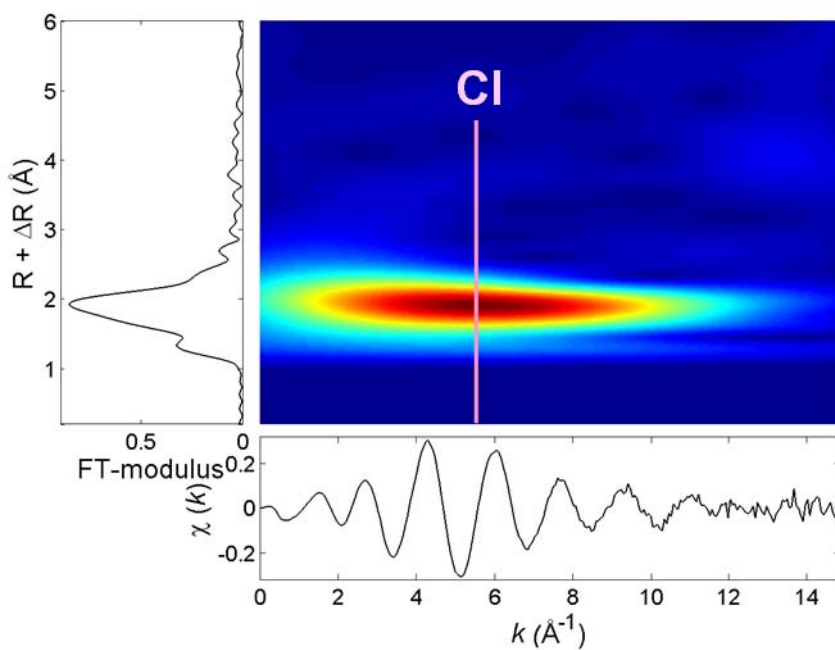


**Fig. EA1-1B**

**exp #5, 0.30m AgCl-5.51m NaCl-0.14m HCl-0.07m H<sub>2</sub>O<sub>2</sub>, 200°C**



**exp #5, 0.30m AgCl-5.51m NaCl-0.14m HCl-0.07m H<sub>2</sub>O<sub>2</sub>, 450°C**

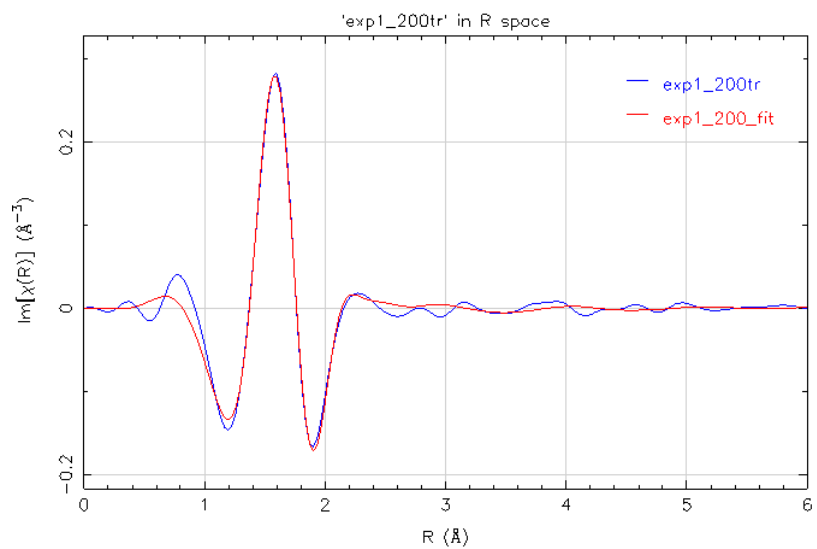
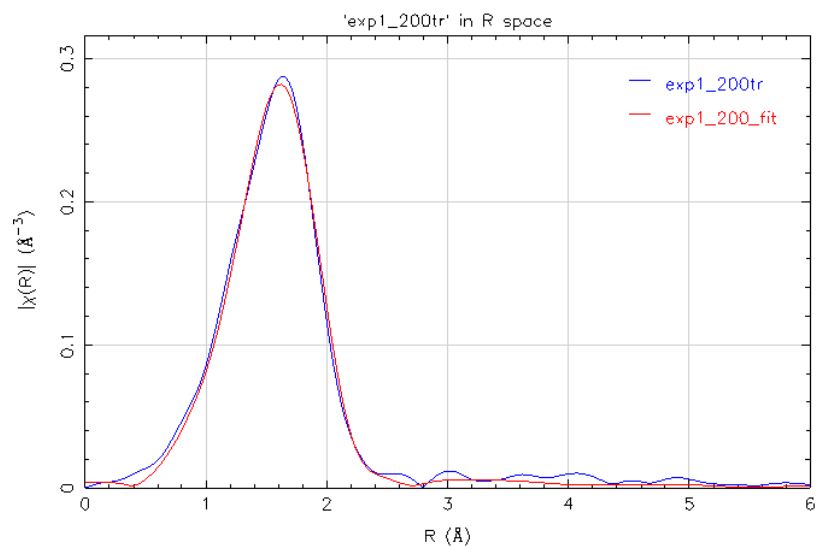
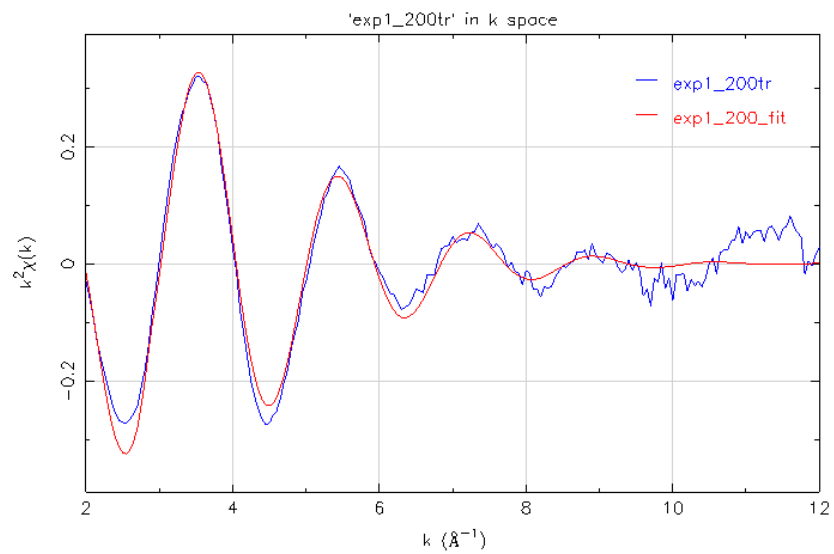


**Fig. EA1-1C**

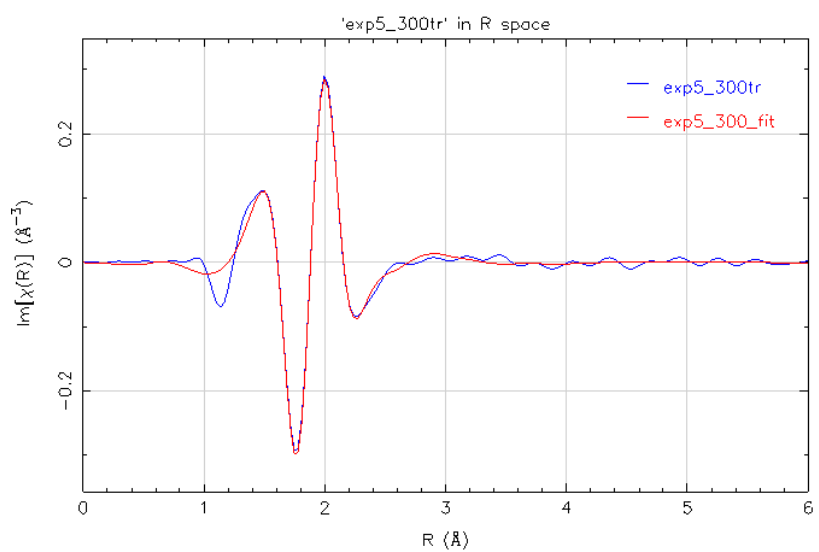
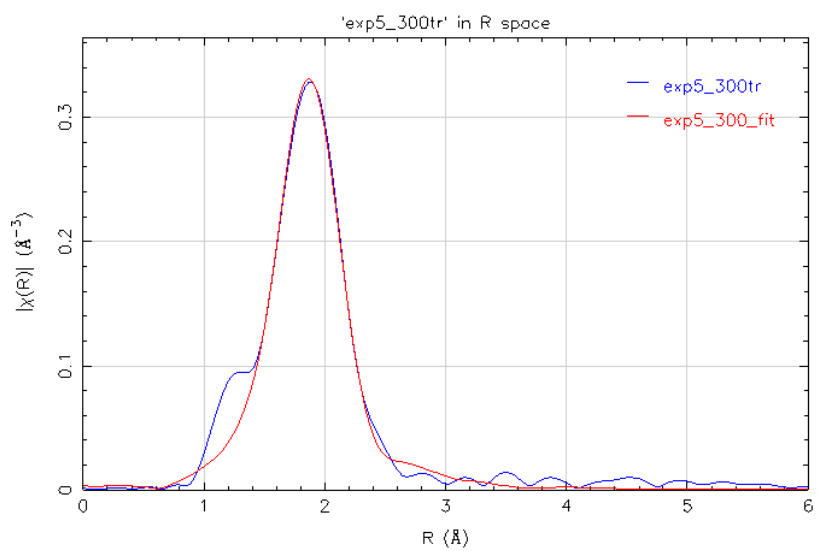
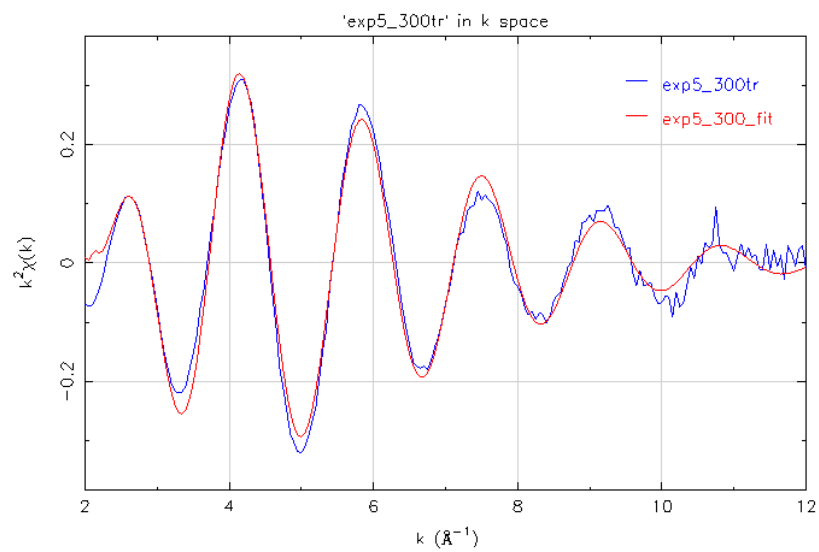
## Electronic annex 2

### Examples of EXAFS fits of representative Ag-chloride and nitrate solutions

**Supplementary Figure EA2-1.** EXAFS fits in  $\chi(k) \times k^2$ -space and R-space (both FT magnitude and imaginary part) of (A) 0.21*m* AgNO<sub>3</sub>-0.1*m* HNO<sub>3</sub>-0.10*m* H<sub>2</sub>O<sub>2</sub> solution (exp #1, 0*m* total Cl) at 200°C/600bar, (B) 0.17*m* AgCl-0.42*m* NaCl-0.11*m* HCl-0.06*m* H<sub>2</sub>O<sub>2</sub> solution (exp #6, 0.70*m* total Cl) at 450°C/700 bar, and (C) 0.30*m* AgCl-5.51*m* NaCl-0.14*m* HCl-0.07*m* H<sub>2</sub>O<sub>2</sub> solution (exp #5, 5.9*m* total Cl) at 300°C/600 bar. For all samples the fitted R-ranges are 1.1-2.8 Å (not corrected for phase shift), and k-ranges are 2.5-10.0 Å<sup>-1</sup> and 3.0-11.8 Å<sup>-1</sup> for nitrate and chloride solutions, respectively. Blue curves = experimental spectrum, red curves = fit.

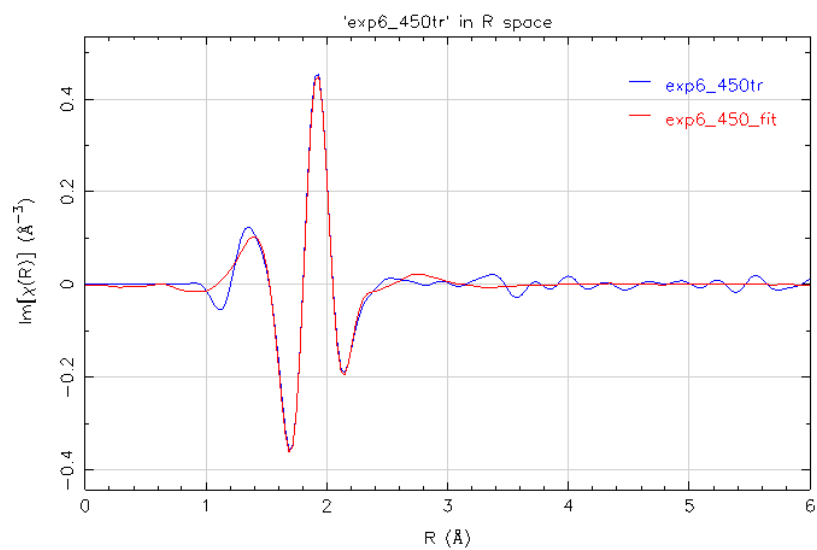
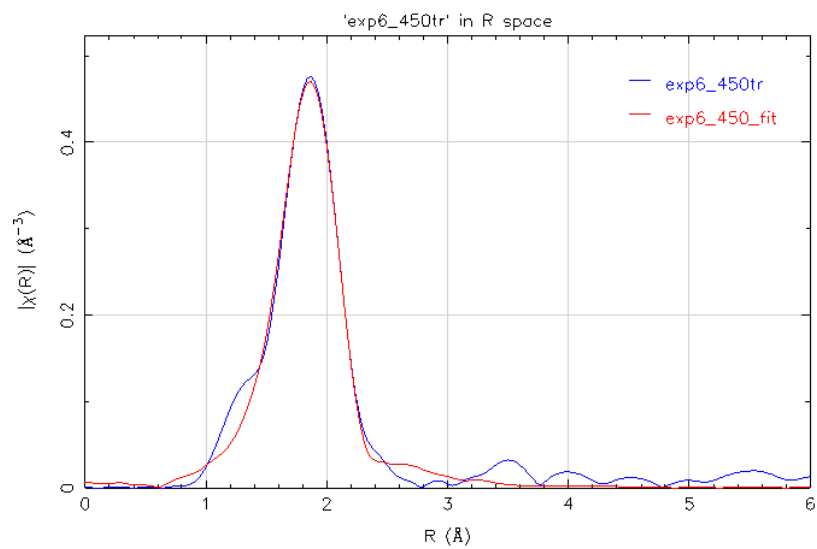
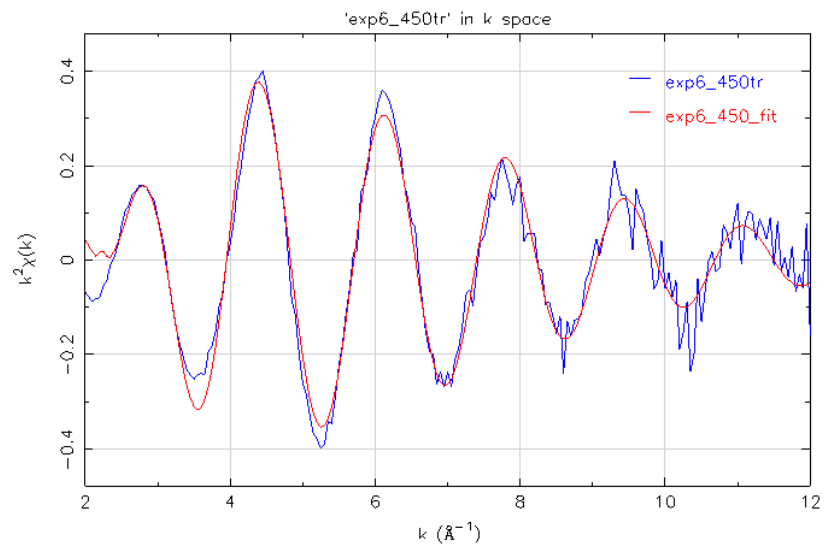


**Fig. EA2-1A, exp #1, 0m Cl<sub>tot</sub>, 200°C/600 bar**



**Fig. EA2-1B, exp #6, 0.70m Cl<sub>tot</sub>, 450°C/700 bar**



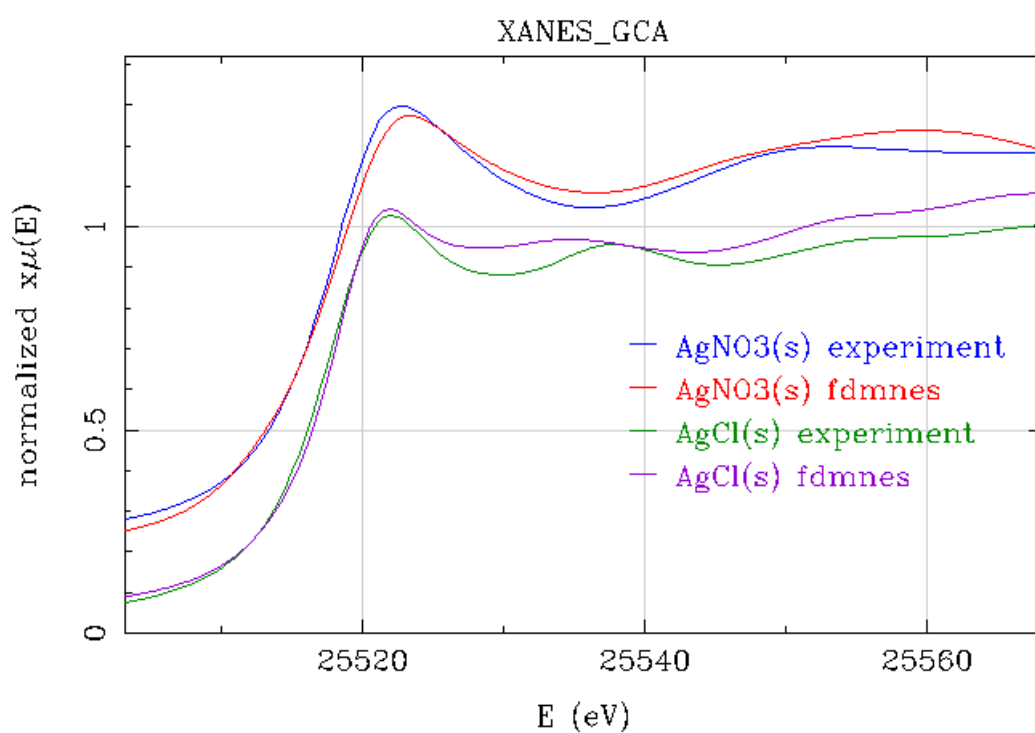


**Fig. EA2-1C, exp #5, 5.9m Cl<sub>tot</sub>, 300°C/600 bar**

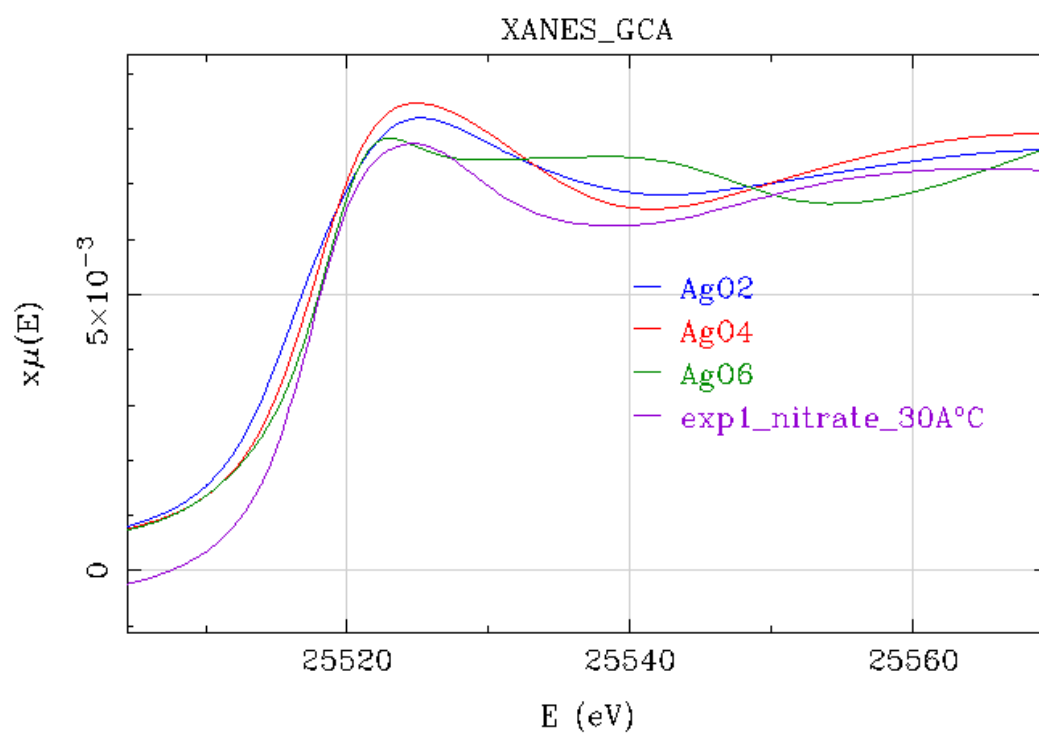
## Electronic annex 3

### Calculated XANES spectra for Ag-bearing solid phases and Ag-O model clusters, and their comparison with experimental data

**Supplementary Figure EA3-1.** Comparison of XANES spectra for silver nitrate and silver chloride solid phases calculated using the FDMNES program and measured in this study.



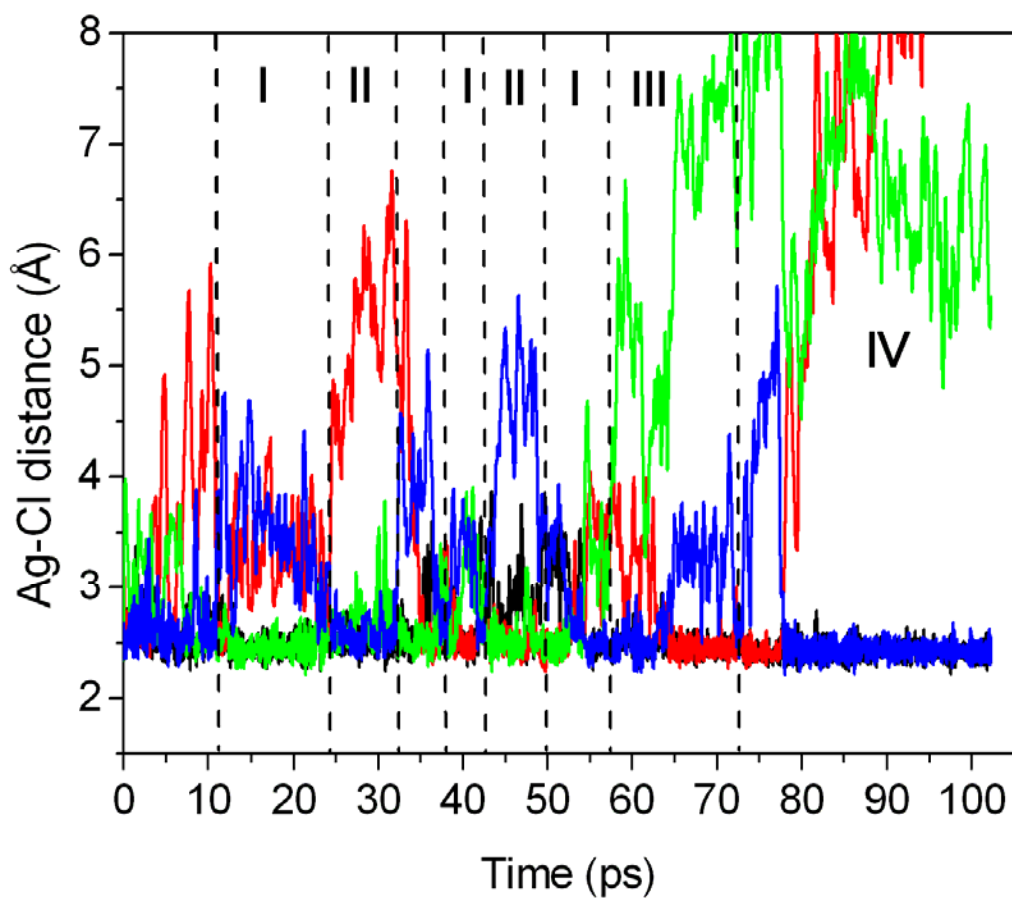
**Supplementary Figure EA3-2.** Comparison of experimental XANES spectra from the Ag-bearing nitrate solution with calculated XANES spectra for representative Ag-O clusters of different geometry and stoichiometry.



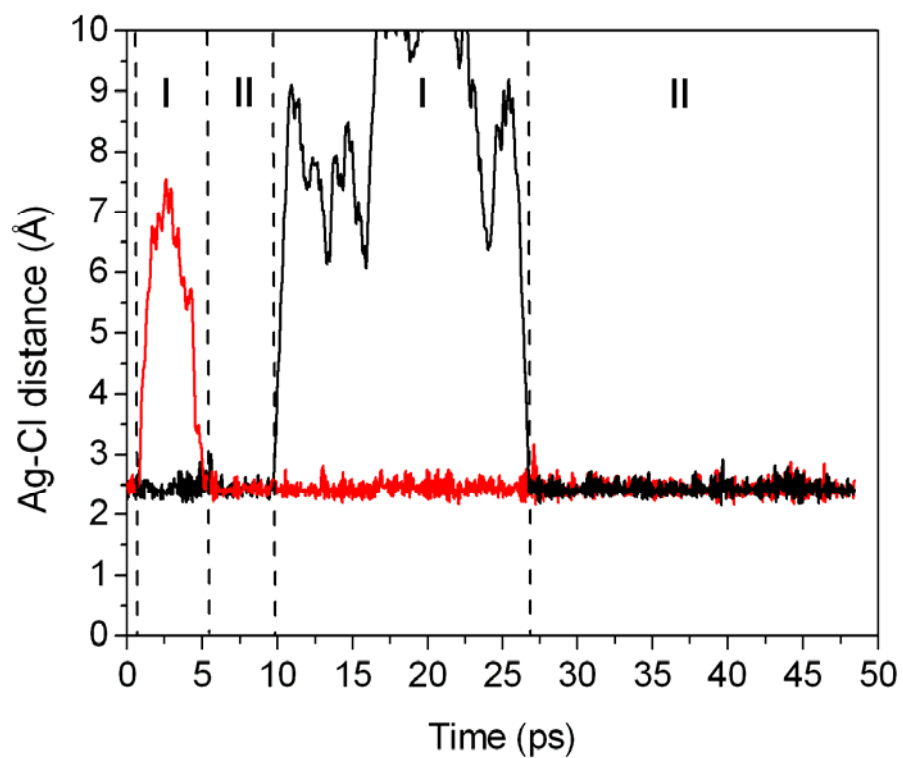
## Electronic annex 4

### Ag-Cl distances as a function of simulation time calculated by molecular dynamics

**Supplementary Figure EA4-1.** Ag-Cl distances as a function of the simulation time (in picosecond) at 50°C calculated for the system containing one  $\text{Ag}^+$ , 4  $\text{Cl}^-$ , and 1  $\text{Na}^+$ . The vertical dotted lines separate regions of time where different types of complexes are identified: I)  $\text{AgCl}_4^{3-}$  II)  $\text{AgCl}_3^{2-}$  III)  $\text{AgCl}_3(\text{H}_2\text{O})^{2-}$  IV)  $\text{AgCl}_2^-$ .



**Supplementary Figure EA4-2.** Ag-Cl distances as a function of the simulation time (in picosecond) at 380°C in the system containing 1 Ag<sup>+</sup>, 2 Cl<sup>-</sup>, and 1 Na<sup>+</sup>. The vertical dotted lines separate regions of time where different types of complexes are identified: I) AgCl(H<sub>2</sub>O), II) AgCl<sub>2</sub><sup>-</sup>.



**Supplementary Figure EA4-3.** Ag-Na radial distribution functions (a) in the system Na-Ag-4Cl at 50°C, 1 bar, and (b) in the system Na-AgCl<sub>2</sub> at 380°C and 600 bar.

